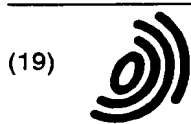


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(54) **PROCESSES FOR PREPARING PESTICIDAL INTERMEDIATES**

VERFAHREN ZUR HERSTELLUNG VON ZWISCHENPRODUKTE FÜR PESTIZIDE

PROCEDES POUR LA PREPARATION DE PRODUITS INTERMEDIAIRES PESTICIDES

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(56) References cited:
EP-A- 0 234 119 EP-A- 0 295 117
WO-A-92/13451 WO-A-93/06089
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29.12.1999 Bulletin 1999/52

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• **Y.H.KIM ET AL: "Novel palladium catalysed
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Description

[0001] This invention relates to processes for preparing pesticidal intermediates, and to novel 2-arylhydrazonosuccinonitrile compounds and to 2-arylhydrazinosuccinonitrile compounds.

[0002] European Patent Publication Nos. 0295117 and 0234119 describe the preparation of pesticidally active phenylpyrazole compounds and of 5-amino-1-aryl-3-cyanopyrazole intermediate compounds used in their synthesis. Various methods for preparing these compounds are known. It is however desirable to provide improved methods for the preparation of these compounds and the intermediate compounds thereto.

[0003] Arylhydrazines are known to undergo Michael addition with electron deficient alkenes such as acrylonitrile in polar protic solvents such as alcohols, and subsequent oxidation in a basic medium affords 5-amino-1-arylpyrazoles as described for example in US Patent Number 4824960. However the applicants are not aware of any literature reports describing the reaction of hydrazines with fumaronitrile. The oxidation of N,N'-diarylhydrazines to azo compounds is known. N-Alkylhydrazines and N-arylhydrazines which are substituted on one nitrogen atom only are also oxidised to azo compounds but these are generally unstable, decomposing to nitrogen and hydrocarbons (see J. March, Advanced Organic Chemistry, 3rd edition, page 1062). Y.H.Kim and Y.Choi describe in Tetrahedron Letters, Vol 37, pages 8771-4, 1996 the palladium catalysed dehydrogenation of alpha-hydrazinonitriles in the presence of cyclopentene to give hydrazonil cyanides. However the applicants are unaware of any other references concerning the oxidation of hydrazines to hydrazones. Moreover, the Kim and Choi publication is restricted to the oxidation of unsubstituted phenyl hydrazine derivatives and no suggestion is made that the oxidation of hydrazine derivatives of fumaronitrile may be achieved.

[0004] It is a first object of the present invention to provide a convenient process for preparing 5-amino-1-aryl-3-cyanopyrazole pesticidal intermediates which are obtained in high yield and high purity.

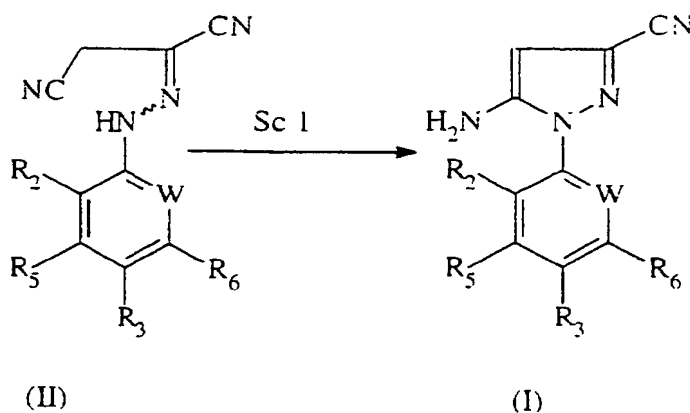
[0005] It is a further object of the present invention to provide processes for the preparation of 2-arylhydrazonosuccinonitrile compounds which may be used to prepare said 5-amino-1-aryl-3-cyanopyrazole pesticidal intermediates.

[0006] It is a yet further object of the present invention to provide a process for the preparation of 2-arylhydrazinosuccinonitrile compounds.

[0007] It is a still further object of the present invention to provide novel intermediates in the manufacture of pesticidally active compounds.

[0008] These and other objects of the invention will become apparent from the following description, and are achieved in whole or in part by the present invention.

[0009] In one aspect the present invention provides a process for the preparation of a compound of formula (I) by the cyclisation of a compound of formula (II), according to the reaction scheme Sc 1 indicated below:



wherein W is nitrogen or -CR₄;

R₂, R₄, R₅ and R₆ are independently selected from hydrogen, halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, R₇S(O)_n, nitro, cyano and -SF₅; and R₃ is as defined for R₂, or is phenyl optionally substituted by one to five members of the group consisting of halogen, alkyl, haloalkyl, alkoxy, haloalkoxy, R₇S(O)_n, nitro, cyano and -SF₅, which may be the same or different;

R₇ is alkyl or haloalkyl; and
n is 0, 1 or 2.

[0010] Unless otherwise specified in the present specification 'alkyl' means straight- or branched- chain alkyl having from one to six carbon atoms (preferably one to three). Unless otherwise specified 'haloalkyl' and 'haloalkoxy' are straight- or branched- chain alkyl or alkoxy respectively having from one to six carbon atoms (preferably one to three) substituted by one or more halogen atoms selected from fluorine, chlorine or bromine.

[0011] Preferred compounds of formula (I) are those having one or more of the following features:- R_2 is halogen or hydrogen; R_3 represents halogen, haloalkyl (preferably trifluoromethyl), haloalkoxy (preferably trifluoromethoxy), $R_7S(O)_p$ -, $-SF_5$, or phenyl substituted by one to three members of the group consisting of trifluoromethyl, trifluoromethoxy, difluoromethyl, $-S(O)_nCF_3$, dichlorofluoromethyl, chlorodifluoromethyl, chlorodifluoromethoxy, dichlorofluoromethoxy and halogen which may be the same or different;

R_4 is halogen; and
 R_5 and R_6 are hydrogen.

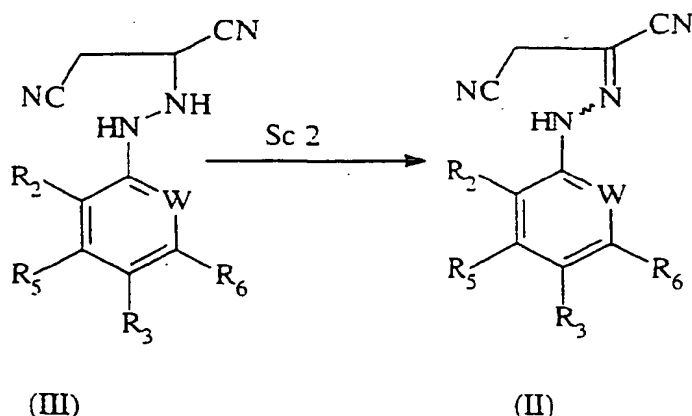
[0012] Especially preferred compounds of formula (I) are those having one or more of the following features:-

W represents $-CR_4$ and R_4 is halogen;
 R_3 represents haloalkyl, haloalkoxy or $-SF_5$; and
 R_5 and R_6 represent hydrogen.

[0013] Most preferably the compound of formula (I) is 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole.

[0014] The above reaction Sc 1 to obtain compounds of formula (I) is generally performed in the presence of a base, which may be organic or inorganic. Examples of suitable organic bases are amines such as triethylamine or pyridine. Examples of suitable inorganic bases are alkali or alkaline earth metal hydroxides, acetates, carbonates or bicarbonates such as sodium hydroxide or sodium carbonate, or preferably ammonia (aqueous or gaseous). Generally the molar ratio of the compound of formula (I):base is from about 1:10, to about 10:1. The reaction is optionally carried out in the presence of a phase transfer catalyst for example quaternary ammonium salts such as benzyl trimethylammonium chloride, tricaprylmethylammonium chloride, tetramethylammonium chloride, tetra-n-propylammonium bromide, n-dodecyl trimethylammonium chloride, tetra-n-butylammonium chloride, and n-tetradecyl trimethylammonium bromide. The reaction is generally performed in a solvent, and suitable solvents include alcohols (preferably ethanol) or non water-miscible solvents, especially halogenated hydrocarbons such as dichloroethane or dichloromethane, non-miscible solvents being appropriate when a phase transfer catalyst is employed. Optionally water may be used as a co-solvent. The reaction temperature is generally from about -20 to about 50°C and preferably from about 0 to about 20°C .

[0015] According to a further feature of the present invention there is provided a process for the preparation of a compound of formula (II) by the oxidation of a compound of formula (III), according to the reaction scheme Sc 2 indicated below:



wherein W, R_2 , R_3 , R_5 and R_6 are as defined above.

[0016] The preferred compounds of formula (II) are as defined for the definition of W, R_2 , R_3 , R_5 and R_6 for compounds of formula (I) above. The most preferred compound of formula (II) is 2-(2,6-dichloro-4-trifluoromethyl-phenylhydrazono) succinonitrile.

[0017] Compounds of formula (II) may be obtained as a mixture of syn and anti isomers and all such forms are

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(II)

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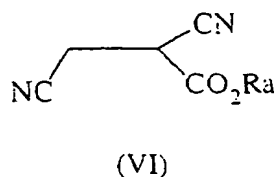
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wherein W, R₂, R₃, R₅ and R₆ have the same meaning as defined above, using conditions known in the literature and generally using a molar equivalent of sodium nitrite and a mineral acid such as hydrochloric acid or sulphuric acid.

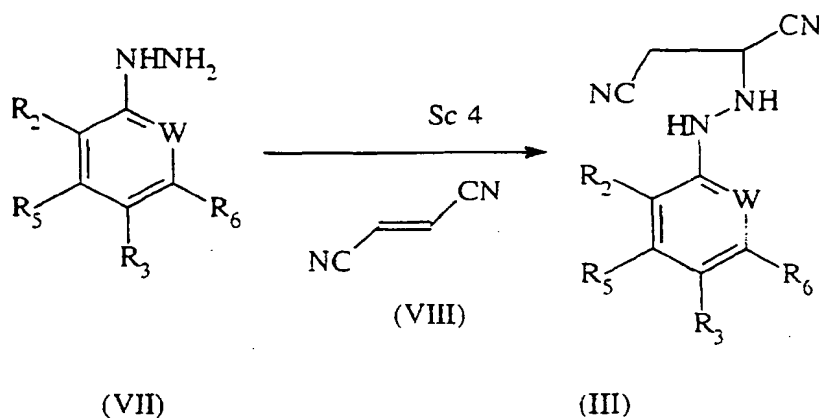
[0022] According to a further feature of the present invention compounds of formula (II) wherein W, R₂, R₃, R₅ and R₆ have the same meaning as defined above in reaction scheme Sc 1 may also be prepared by the reaction of a compound of formula (VI):



wherein Ra is alkyl preferably ethyl, with a diazonium salt of formula (V) wherein W, R₂, R₃, R₅, R₆ and X are as defined above

[0023] The reaction conditions used are the same as those described above for reaction scheme Sc 3 above.

[0024] According to a further feature of the present invention compounds of formula (III) above may be prepared by the reaction of an arylhydrazine of formula (VII) with a compound of formula (VIII), according to reaction scheme Sc 4 indicated below.



wherein W, R₂, R₃, R₅ and R₆ have the same meanings as defined above in reaction scheme Sc 1.

[0025] Compounds of formula (VIII) are known and may be used in the form of the cis-isomer maleonitrile or preferably the trans isomer fumaronitrile. Optionally a mixture of both isomers may be used. Arylhydrazines of formula (VII) are known or may be prepared by known methods.

[0026] Preferred compounds of formula (III) have the same values of W, R₂, R₃, R₅ and R₆ as preferred above for compounds of formula (I). Most preferably the compound of formula (III) is 2-(2,6-dichloro-4-trifluoromethylphenylhydrazino)succinonitrile.

[0027] The above reaction to form compounds of formula (III) may be performed in a variety of solvents, polar solvents being preferred, for example alcohols. Polar aprotic solvents such as N-methylpyrrolidone, N,N-dimethylformamide or dimethylsulphoxide are especially preferred. In another preferred aspect the reaction is performed in the absence of solvent by heating a mixture of compounds of formula (VII) and (VIII).

[0028] Optionally a catalyst such as a tetra-alkylammonium salt for example N-benzyltrimethylammonium hydroxide, or alanine may also be present in the reaction.

[0029] The reaction temperature is generally from about 20 to about 150°C, and preferably from about 80 to about 100°C.

[0030] The reaction may be carried out using a molar ratio of a compound of formula (VIII) to a compound of formula (VII) of from about 1:10 to about 10:1, and preferably from about 1:1 to about 5:1, even more preferably about 1.1 to 1.

[0031] Compounds of formula (II) and (III) above are novel and therefore constitute a further feature of the present invention.

[0032] The following non-limiting examples illustrate the invention. NMR spectra are recorded using deuteriochloro-

form as solvent. Hplc means high performance liquid chromatography, m.p. means melting point.

Example 1

[0033] Preparation of 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole (Reaction scheme Sc 1)
[0034] Ammonia (20 microlitres of an 8% ammonia solution in water) was added to a mixture of 2-(2,6-dichloro-4-trifluoromethylphenylhydrazono)succinonitrile (0.077g) in ethanol (1ml) and water (0.2ml) at 0°C. After 10 minutes the mixture was extracted (dichloromethane) and evaporated to give the title compound (0.076g, 97% yield). Purity 98% (by hplc).

Example 2

[0035] Preparation of 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole (Reaction scheme Sc 1)
[0036] A solution of 2-(2,6-dichloro-4-trifluoromethylphenylhydrazono)succinonitrile (1.0g) and sodium bicarbonate (40ml of a saturated aqueous solution) and dichloromethane (15ml) was stirred at 20°C for 3 hours at pH 9. Sodium carbonate solution was then added until the pH was 11 and the stirring continued overnight. A small amount of sodium hydroxide solution was added to give a pH of 12, followed three hours later by a small quantity of Aliquat 336 (trademark, tricaprylmethylammonium chloride), and after 2 hours the reaction was complete. A dichloromethane extract was washed (water and brine), dried (sodium sulphate) and evaporated to give the title compound.

Example 3

Preparation of 2-(2,6-dichloro-4-trifluoromethylphenylhydrazono)succinonitrile (Reaction Scheme Sc 2)

[0037] A mixture of 2-(2,6-dichloro-4-trifluoromethylphenylhydrazino)succinonitrile (0.323g) and cupric chloride (0.175g) was heated in chlorobenzene at 60°C for 6 hours. After filtration and evaporation the title compound and 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole were obtained as a 7:1 mixture. Column chromatography on silica gel eluting with dichloromethane gave the pure title compound, obtained as a mixture of syn and anti isomers, NMR (anti isomer) 3.6(s,2H), 7.57(s,2H), 8.82(s,1H, exchangeable with D₂O), NMR (syn isomer) 3.56(s,2H), 7.59(s,2H), 8.27(s,1H, exchangeable with D₂O).

Example 4

Preparation of 2-(2,6-dichloro-4-trifluoromethylphenylhydrazono)succinonitrile (Reaction scheme Sc 3)

[0038] Sodium nitrite (3.9g) was added to stirred concentrated sulphuric acid (12.8ml) and heated at 80°C until dissolved. Acetic acid (25ml) was added at 30°C. A mixture of 2,6-dichloro-4-trifluoromethylphenylaniline (10.0g) and acetic acid (25ml) was added over 10 minutes at 20°C maintaining below 25°C. The mixture was heated at 55°C for 50 minutes, and further sodium nitrite (0.65g) and acetic acid (10ml) added, and after 20 minutes heated to 70°C and sulphuric acid (2.8ml) added. After 20 minutes the cooled mixture was added to a mixture of 2-hydroxymethylenesuccinonitrile potassium salt (7.6g) and sodium acetate (35.6g) in water and acetic acid (70ml) at 10°C. After warming to 20°C during 1 hour, dichloromethane was added followed by ammonium hydroxide solution (210ml) to give a pH of 8. The organic phase was separated, washed (water and brine), dried (sodium sulphate) and evaporated to give the title compound as a red brown solid (18.1g). Recrystallisation from hexane/t-butyl methylether gave the pure title compound (6.85g), m.p. 80-82°C, NMR 3.6(s,2H), 7.66(s,2H), 9.03(s,1H exchangeable with D₂O).

Example 5

Preparation of 2-(2,6-dichloro-4-trifluoromethylphenylhydrazino)succinonitrile (Reaction Scheme Sc 4)

[0039] A mixture of 2,6-dichloro-4-trifluoromethylphenylhydrazine (1.0g) and fumaronitrile (1.0g) in dimethylsulphoxide (10ml) was heated at 100°C for 7 hours. The cooled mixture was diluted with water and extracted (ether) to give, after evaporation and crystallisation from dichloromethane/hexane, the title compound (0.828g, 63%), m.p. 101-102°C.

Example 6

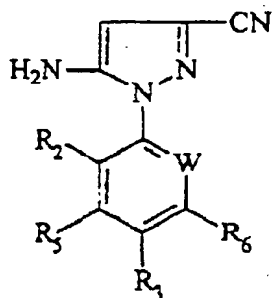
Preparation of 2-(phenylhydrazino)succinonitrile (Reaction Scheme Sc 4)

[0040] A mixture of phenylhydrazine (4.29g) and fumaronitrile (3.1g), where the phenylhydrazine served as a solvent, was heated at 75-80°C for 20 hours. Purification by flash chromatography on silica gel and crystallisation from dichloromethane/hexane gave the title compound (3.29g, 45%), m.p.97-98°C.

[0041] While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions and changes can be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims, including equivalents thereof.

Claims

1. A process for the preparation of a compound of formula (I)

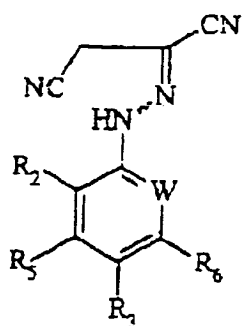


(I)

wherein W is nitrogen or -CR₄;

R₂, R₄, R₅ and R₆ are independently selected from hydrogen, halogen, C₁₋₆ alkyl, C₁₋₆ haloalkyl, C₁₋₆ alkoxy, C₁₋₆ haloalkoxy, R₇S(O)_n-, nitro, cyano and -SF₅;
and R₃ is hydrogen, halogen, C₁₋₆ alkyl, C₁₋₆ haloalkyl, C₁₋₆ alkoxy, C₁₋₆ haloalkoxy, R₇S(O)_n-, nitro, cyano, -SF₅, or phenyl substituted by one to five members of the group consisting of halogen, C₁₋₆ alkyl, C₁₋₆ haloalkyl, C₁₋₆ alkoxy, C₁₋₆ haloalkoxy, R₇S(O)_n-, nitro, cyano and -SF₅, which may be the same or different;
R₇ is C₁₋₆ alkyl or C₁₋₆ haloalkyl; and
n is 0, 1 or 2;

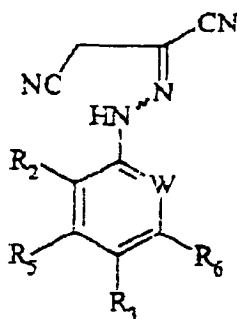
which comprises the cyclization, in the presence of a base, of a compound of formula (II):



(II)

wherein W, R₂, R₃, R₅ and R₆ are as defined above.

2. A process according to Claim 1 in which the molar ratio of base:compound of formula (II) is from about 1:10 to about 10 : 1
3. A compound having the formula (II):



(II)

wherein W, R₂, R₃, R₅ and R₆ are as defined in Claim 1.

4. A compound according to Claim 3 which has one or more of the following features:

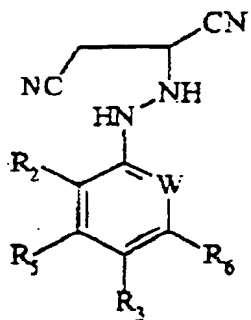
R₂ is halogen or hydrogen;

R₃ represents halogen, C₁₋₆ haloalkyl, C₁₋₆ haloalkoxy, R₇S(O)_p⁻, -SF₅, or phenyl substituted by one to three members of the group consisting of trifluoromethyl, trifluoromethoxy, difluoromethyl, -S(O)_nCF₃, dichlorofluoromethyl, chlorodifluoromethyl, chlorodifluoromethoxy, dichlorofluoromethoxy and halogen, which may be the same or different;

R₄ is halogen;

R₅ and R₆ are hydrogen.

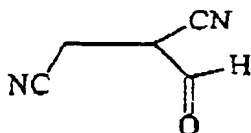
5. A process for the preparation of a compound of formula (II) as defined in Claim 3, said process comprising the oxidation of a compound having the formula (III):



(III)

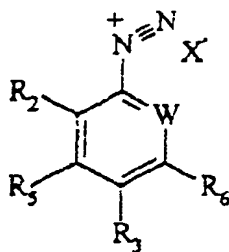
wherein W , R_2 , R_3 , R_5 and R_6 are as defined in Claim 3, using an oxidant,

6. A process according to Claim 5 in which the oxidant is selected from a quinone; a peroxide; a hypohalite; an alkali metal hydroxide in the presence of air; a metal salt and a metal oxide.
7. A process for the preparation of a compound of formula (II) as defined in Claim 3, said process comprising the reaction of an enolate salt of a compound having the formula (IV):



(IV)

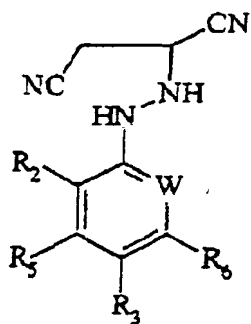
with a diazonium salt having the formula (V)



(V)

wherein W , R_2 , R_3 , R_5 and R_6 are as defined in Claim 3 and X is hydrogen sulphate or chloride.

8. A compound having the formula (III):



(III)

wherein W, R₂, R₃, R₅ and R₆ are as defined in Claim 1.

9. A compound according to Claim 8 which has one or more of the following features:

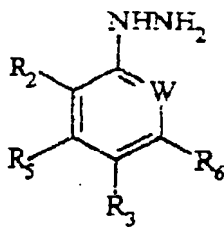
R₂ is halogen or hydrogen;

R₃ represents halogen, C₁₋₆ haloalkyl, C₁₋₆ haloalkoxy, R₇S(O)_p, -SF₅, or phenyl substituted by one to three members of the group consisting of trifluoromethyl, trifluoromethoxy, difluoromethyl, -S(O)_nCF₃, dichlorofluoromethyl, chlorodifluoromethyl, chlorodifluoromethoxy, dichlorofluoromethoxy and halogen, which may be the same or different;

R₄ is halogen;

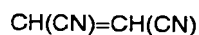
R₅ and R₆ are hydrogen.

10. A process for the preparation of a compound of formula (III) as defined in Claim 8, said process comprising the reaction of an arylhydrazine having the formula (VII):



(VII)

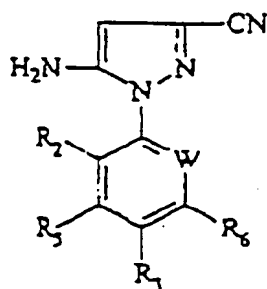
wherein W, R₂, R₃, R₅ and R₆ are as defined in Claim 8, with a compound of formula (VIII):



(VIII).

Patentansprüche

1. Ein Verfahren zur Herstellung einer Verbindung der Formel (I)



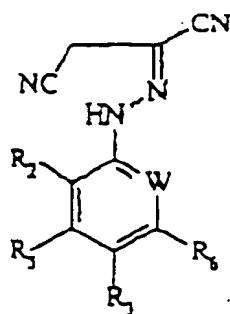
(I)

worin W Stickstoff oder $-CR_4$ ist;

R_2 , R_4 , R_5 und R_6 unabhängig voneinander ausgewählt werden aus Wasserstoff, Halogen, C_{1-6} -Alkyl, C_{1-6} -Halogenalkyl, C_{1-6} -Alkoxy, C_{1-6} -Halogenalkoxy, $R_7S(O)_n$, Nitro, Cyano und $-SF_5$; und R_3 Wasserstoff, Halogen, C_{1-6} -Alkyl, C_{1-6} -Halogenalkyl, C_{1-6} -Alkoxy, C_{1-6} -Halogenalkoxy, $R_7S(O)_n$, Nitro, Cyano, $-SF_5$ oder ein Phenyl ist, welches mit einem bis fünf Elementen der Gruppe bestehend aus Halogen, C_{1-6} -Alkyl, C_{1-6} -Halogenalkyl, C_{1-6} -Alkoxy, C_{1-6} -Halogenalkoxy, $R_7S(O)_n$, Nitro, Cyano und $-SF_5$ substituiert ist, wobei diese gleich oder verschieden sein können;

R_7 C_{1-6} -Alkyl oder C_{1-6} -Halogenalkyl ist; und n 0, 1 oder 2 ist;

welches die Cyclisierung, in Gegenwart einer Base, einer Verbindung der Formel (II) :

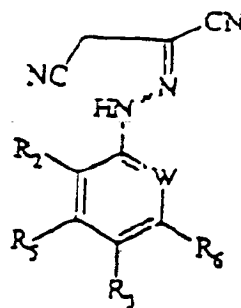


(II)

umfaßt, worin W, R_2 , R_3 , R_5 und R_6 so sind wie oben definiert.

2. Ein Verfahren gemäß Anspruch 1, bei welchem das Molverhältnis von Base : Verbindung der Formel (II) von ca. 1:10 bis ca. 10:1 beträgt.

3. Eine Verbindung mit der Formel (II):



(II)

worin W , R_2 , R_3 , R_5 und R_6 so sind wie in Anspruch 1 definiert.

4. Eine Verbindung gemäß Anspruch 3, welche eines oder mehrere der folgenden Merkmale aufweist:

R_2 ist Halogen oder Wasserstoff;

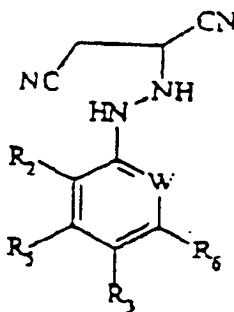
R_3 steht für Halogen, C_{1-6} -Halogenalkyl, C_{1-6} -Halogenalkoxy, $R_7S(O)_p$, $-SF_5$ oder ein Phenyl, das mit einem bis drei

Elementen der Gruppe bestehend aus Trifluormethyl, Trifluormethoxy, Difluormethyl, $-S(O)_nCF_3$, Dichlorfluormethyl, Chlordifluormethyl, Chlordifluormethoxy, Dichlorfluormethoxy und Halogen substituiert ist, welche gleich oder verschieden sein können;

R_4 ist Halogen,

R_5 und R_6 sind Wasserstoff.

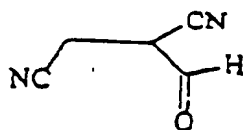
5. Ein Verfahren zur Herstellung einer Verbindung der Formel (II) wie in Anspruch 3 definiert, wobei das Verfahren die Oxidation einer Verbindung mit der Formel (III):



(III)

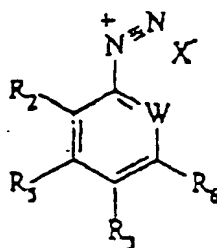
umfaßt, worin W , R_2 , R_3 , R_5 und R_6 so sind wie in Anspruch 3 definiert, wobei ein Oxidationsmittel verwendet wird.

6. Ein Verfahren gemäß Anspruch 5, bei welchem das Oxidationsmittel ausgewählt ist aus einem Chinon; einem Peroxid; einem Hypohalogenit; einem Alkalimetallhydroxid in Gegenwart von Luft; einem Metallsalz und einem Metalloxid.
7. Ein Verfahren zur Herstellung einer Verbindung der Formel (II) wie in Anspruch 3 definiert, wobei das Verfahren die Reaktion eines Enolatsalzes einer Verbindung mit der Formel (IV):



(IV)

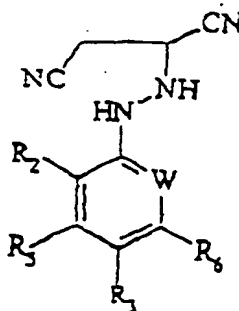
mit einem Diazoniumsalz mit der Formel (V)



(V)

umfaßt, wobei W, R₂, R₃, R₅ und R₆ so sind wie in Anspruch 3 definiert und X Schwefel- oder Salzsäure ist.

8. Eine Verbindung mit der Formel (III):



(III)

worin W, R₂, R₃, R₅ und R₆ so sind wie in Anspruch 1 definiert.

9. Eine Verbindung gemäß Anspruch 8, welche eines oder mehrere der folgenden Merkmale aufweist:

R₂ ist Halogen oder Wasserstoff;

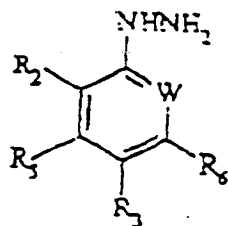
R₃ steht für Halogen, C₁₋₆-Halogenalkyl, C₁₋₆-Halogenalkoxy, R₇S(O)_p-, -SF₅ oder ein Phenyl, das mit einem bis drei Elementen aus der Gruppe bestehend aus Trifluormethyl, Trifluormethoxy, Difluormethyl, -S(O)_nCF₃, Dichlorfluormethyl, Chlordifluormethyl, Chlordifluormethoxy, Dichlorfluormethoxy und Halogen substituiert ist, welche gleich oder verschieden sein können;

R₄ ist Halogen;

R₅ und R₆ sind Wasserstoff.

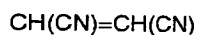
10. Ein Verfahren zur Herstellung einer Verbindung der Formel

(III) wie in Anspruch 8 definiert, wobei das Verfahren die Reaktion eines Arylhydrazins mit der Formel (VII):



(VII)

worin, W, R₂, R₃, R₅ und R₆ so wie in Anspruch 8 definiert sind, mit einer Verbindung der Formel (VIII):

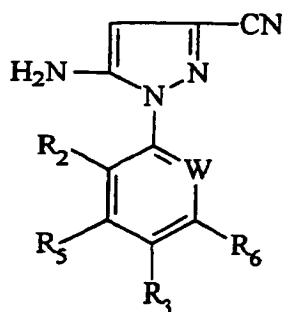


(VIII)

umfaßt.

Revendications

1. Procédé de préparation d'un composé de formule (I)



(I)

dans laquelle :

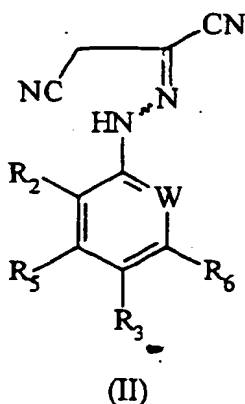
W représente l'atome d'azote ou -CR₄ ;

R₂, R₄, R₅ et R₆ sont indépendamment choisis parmi l'atome d'hydrogène, les atomes d'halogènes, un radical alkyle en C₁₋₆, un radical haloalkyle en C₁₋₆, un radical alkoxy en C₁₋₆, un radical haloalkoxy en C₁₋₆, R₇S(O)_n⁻, nitro, cyano et -SF₅ ;

et R₃ représente l'atome d'hydrogène, les atomes d'halogènes, un radical alkyle en C₁₋₆, un radical haloalkyle en C₁₋₆, un radical alkoxy en C₁₋₆, un radical haloalkoxy en C₁₋₆, R₇S(O)_n⁻, nitro, cyano, -SF₅, ou un radical phényle substitué par un à cinq membres d'un groupe consistant en les atomes d'halogènes, un radical alkyle en C₁₋₆, un radical haloalkyle en C₁₋₆, un radical alkoxy en C₁₋₆, un radical haloalkoxy en C₁₋₆, R₇S(O)_n⁻, nitro, cyano et -SF₅, qui peuvent être identiques ou différents ;

R₇ représente un radical alkyle en C₁₋₆ ou un radical haloalkyle en C₁₋₆; et n représente 0, 1 ou 2 ;

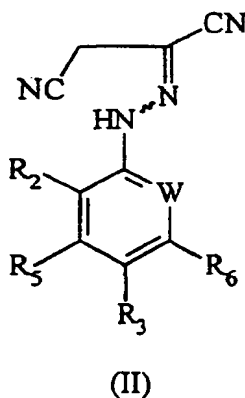
lequel procédé comprend la cyclisation, en présence d'une base, d'un composé de formule (II) :



dans laquelle :

W, R₂, R₃, R₅ et R₆ sont tels que définis précédemment.

2. Procédé selon la revendication 1 dans laquelle le ratio molaire de base/composé de formule (II) est compris entre environ 1:10 et environ 10:1.
3. Composé répondant à la formule (II) :



dans laquelle :

W, R₂, R₃, R₅ et R₆ sont tels que définis dans la revendication 1.

4. Composé selon la revendication 3 qui possède une ou plusieurs des caractéristiques suivantes :

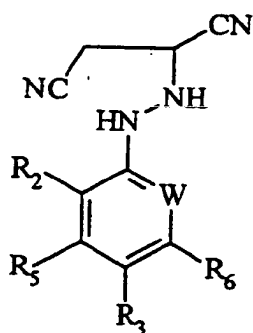
R₂ représente un atome d'halogènes ou l'atome d'hydrogène ;

R₃ représente un atome d'halogènes, un radical haloalkyle en C₁₋₆, un radical haloalkoxy en C₁₋₆, R₇S(O)_p, -SF₅, ou un radical phényle substitué par un à trois membres d'un groupe consistant en trifluorométhyle, trifluorométhoxy, difluorométhyle, -S(O)_nCF₃, dichlorofluorométhyle, chlorodifluorométhyle, chlorodifluorométhoxy, dichlorofluorométhoxy et les atomes d'halogènes, qui peuvent être identiques ou différents ;

R₄ représente un atome d'halogènes ;

R₅ et R₆ représentent l'atome d'hydrogène.

5. Procédé de préparation d'un composé de formule (II) telle que définie dans la revendication 3, le dit procédé comprenant l'oxydation d'un composé répondant à la formule (III) :

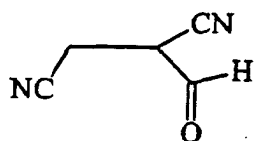


(III)

dans laquelle :

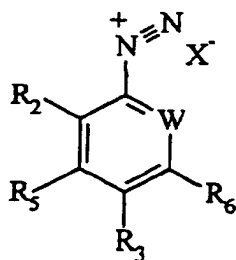
W, R₂, R₃, R₅ et R₆ sont tels que définis dans la revendication 3, en utilisant un oxydant.

6. Procédé selon la revendication 5 dans laquelle l'oxydant est choisi parmi une quinone; un peroxide; un hypo-halogénite; un hydroxyde de métal alcalin en présence d'air, un sel métallique et un oxyde métallique.
7. Procédé de préparation d'un composé de formule (II) telle que définie dans la revendication 3, le dit procédé comprenant la réaction d'un sel énoate d'un composé répondant à la formule (IV):



(IV)

avec un sel de diazonium répondant à la formule (V) :

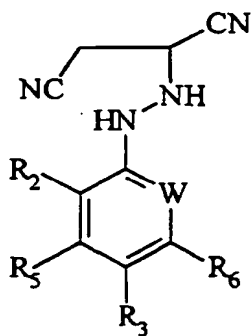


(V)

dans laquelle :

W, R₂, R₃, R₅ et R₆ sont tels que définis dans la revendication 3 et X représente le sulfate ou le chlorure d'hydrogène.

8. Composé répondant à la formule (III) :



(III)

dans laquelle :

W, R₂, R₃, R₅ et R₆ sont tels que définis dans la revendication 1.

9. Composé selon la revendication 8 qui possède une ou plusieurs des caractéristiques suivantes :

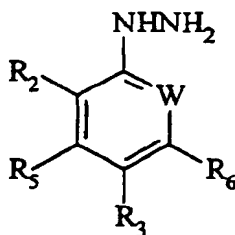
R₂ représente un atome d'halogènes ou l'atome d'hydrogène ;

R₃ représente un atome d'halogènes, un radical haloalkyle en C₁₋₆, un radical haloalkoxy en C₁₋₆, R₇S(O)_p-, -SF₅, ou un radical phényle substitué par un à trois membres d'un groupe consistant en trifluorométhyle, trifluorométhoxy, difluorométhyle, -S(O)_nCF₃, dichlorofluorométhyle, chlorodifluorométhyle, chlorodifluorométhoxy, dichlorofluorométhoxy et les atomes d'halogènes, qui peuvent être identiques ou différents ;

R₄ représente un atome d'halogènes ;

R₅ et R₆ représentent l'atome d'hydrogène.

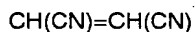
10. Procédé de préparation d'un composé de formule (III) telle que définie dans la revendication 8, le dit procédé comprenant la réaction d'une arylhydrazine répondant à la formule (VII) :



(VII)

dans laquelle :

W, R₂, R₃, R₅ et R₆ sont tels que définis dans la revendication 8, avec un composé de formule (VIII):



(VIII).

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